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TECHNICAL REPORT NO. 45

The Role of Solvent Reorganization Dynamics in Electron-  
Transfer Processes. Theory-Experiment Comparisons  
For Electrochemical and Homogeneous Electron Exchange  
Involving Metallocene Redox Couples

by

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Prepared for Publication

in the

Journal of Physical Chemistry

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August 1985

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER	
Technical Report No. 45	AD-A160034		
4. TITLE (and Subtitle)		5. TYPE OF REPORT & PERIOD COVERED	
The Role of Solvent Reorganization Dynamics in Electron-Transfer Processes. Theory-Experiment Comparisons For Electrochemical and Homogeneous Electron Exchange Involving Metallocene Redox Couples.		Technical Report No. 45	
7. AUTHOR(s)		6. PERFORMING ORG. REPORT NUMBER	
Thomas Gennett, David F. Milner, and Michael J. Weaver			
9. PERFORMING ORGANIZATION NAME AND ADDRESS		8. CONTRACT OR GRANT NUMBER(s)	
Department of Chemistry Purdue University West Lafayette, IN 47907		N00014-79-C-0670	
11. CONTROLLING OFFICE NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
Office of Naval Research Department of the Navy Arlington, VA 22217			
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE	
		August 1985	
		13. NUMBER OF PAGES	
		15. SECURITY CLASS. (of this report)	
		Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report)		Accession For	
Approved for Public Release; distribution unlimited		NTIS CRA&I <input checked="" type="checkbox"/>	
		DTIC TAB <input type="checkbox"/>	
		Unannounced <input type="checkbox"/>	
		Justification	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		Block 5 large changed	
		By <i>metalsmith, J.C.</i>	
		Distribution/	
		Availability Codes	
18. SUPPLEMENTARY NOTES		Dist	
		Avail and/or Special	
		A1	
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)			
Electrochemical Rate Constants, Activation Parameters, metallocene couples			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)			
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FOR ELECTROCHEMICAL AND HOMOGENEOUS ELECTRON EXCHANGE  
INVOLVING METALLOCENE REDOX COUPLES.

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Abstract

Electrochemical Rate Constants and Activation Parameters are reported for the electron exchange of five metallocene couples and dibenzenechromium(I)/(0) in eight solvents at mercury electrodes. The solvents (acetonitrile, acetone, methylene chloride, formamide, N-methylformamide, N,N'-dimethylformamide, dimethylsulfoxide, and benzonitrile) were chosen so to provide substantial variations in their dynamical as well as dielectric properties. The metallocene couples are of the form  $M(Cp)_2^{(+/0)}$ , where  $M = Fe, Co, \text{ or } Mn$ , and  $Cp =$  cyclopentadiene or pentamethylcyclopentadiene. The inner-shell (i.e., bond distortional) barriers are calculated for the metallocene and arene couples from bond-distance and vibrational data to be small (~~or approx.~~  $\sim 0.25 \text{ kcal/mol}$ ) yet metal-dependent. Detailed comparisons of the observed solvent-dependent kinetics are made with the rate parameters calculated from contemporary theoretical treatments of outer-sphere electron transfer. Considerably better agreement between the experimental and theoretical kinetic parameters was obtained when the latter take into account the influence of solvent friction upon the barrier-crossing frequency. A comparison between the corresponding experimental and theoretical rate parameters for ferricinium-ferrocene self exchange in eight solvents yielded a similar finding. These results indicate that the conventional transition-state theory may not apply to electron-transfer reactions where the free-energy barrier is due chiefly to solvent reorganization, at least in "high friction" media where concerted solvent relaxation is slow. The likely influences of the solvent upon the kinetics of other outer-sphere reactions is also discussed in the light of these findings.

A particularly interesting class of condensed-phase reactions is provided by electron exchange involving redox couples with little or no molecular structural changes, since the kinetics will be determined largely by solvent reorganization. Detailed examination of such processes as a function of solvent properties can therefore provide direct tests of the solvent reorganization energetics as described by contemporary theoretical models.<sup>1,2</sup> An intriguing recent development concerns the emergence of detailed theoretical treatments of solvent reorganization dynamics in condensed-phase reactions,<sup>2</sup> including electron transfer.<sup>2a-c</sup> These models predict that the dynamical, as well as dielectric, solvent properties can exert a dominant influence upon the barrier-crossing rates.<sup>2</sup>

Experimental work has focussed attention on electron exchange of aromatic molecule-radical anion redox couples in homogeneous aprotic media<sup>3</sup> and at electrochemical interfaces,<sup>4</sup> although few studies have been concerned with detailed solvent effects. Another class of such reactions involves organometallic complexes, especially those containing aromatic groups such as cyclopentadienyl and arene ligands. A number of these complexes exhibit reversible one-electron reduction or oxidation in a wide variety of solvents, with only minor changes in metal-ligand bond lengths attending electron transfer so that the inner-shell activation energies are small ( $\leq 0.3 \text{ kcal mol}^{-1}$ ), yet variable. In addition, these reactions commonly involve either uncharged or singly charged reactants and products, thereby minimising the influence of electrostatic work terms on the measured kinetics. Nevertheless, surprisingly few studies of their electron-transfer kinetics have been undertaken.<sup>5</sup>

In the present paper, we report standard electrochemical rate constants and activation parameters extracted from a.c. impedance measurements for ferricinium-ferrocene, manganicinium-manganocene, cobalticinium-cobaltocene, and

dibenzo-chromium(I)/(0) couples, at a mercury electrode in dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), N-methylformamide (NMF), formamide, acetonitrile, acetone, methylene chloride ( $\text{CH}_2\text{Cl}_2$ ), and benzonitrile. A preliminary account is also available.<sup>6</sup> These solvents were selected on the basis of their well-defined electrochemical behavior, and to provide a variety of dielectric and dynamical environments (*vide infra*). Although standard rate constants for ferricinium-ferrocene in nonaqueous media have been reported recently by several workers,<sup>7</sup> these values were obtained at solid surfaces using techniques under conditions where the quantitative validity of the derived rates is questionable.<sup>8</sup>

A major factor leading us to select such couples for detailed study is the availability of solvent-dependent rate parameters for homogeneous self exchange of ferricinium-ferrocene  $[\text{Fe}(\text{Cp})_2]^{+/0}$ , Cp = cyclopentadiene] and for several methyl derivatives.<sup>4</sup> Although the formal potential for ferricinium-ferrocene itself is inconveniently close to the anodic limit in most solvents at mercury, the decamethyl derivative  $[\text{Fe}(\text{Cp}')_2]^{+/0}$ , where Cp' = permethylcyclopentadiene] exhibits formal potentials that are close to the potentials of zero charge, thereby minimising work-term ("double layer") effects. Besides the latter couple, electrochemical rate parameters were obtained in each solvent for  $\text{Mn}(\text{Cp}')_2^{+/0}$ ,  $\text{Co}(\text{Cp}')_2^{+/0}$ ,  $\text{Co}(\text{Cp})_2^{+/0}$  and  $\text{Cr}(\text{C}_6\text{H}_6)_2^{+/0}$ . All of these couples have small or negligible inner-shell barriers as derived from known structural parameters; they nevertheless exhibit widely different formal potentials that enable the possible influence of the double layer on the rate parameters to readily be assessed.

The present study constitutes the first systematic evaluation of electrochemical reactivities for metallocene and arene species. The comparisons presented herein with corresponding homogeneous reactivities and with rate

parameters obtained from contemporary theory demonstrate the significance of solvent reorganization dynamics to such simple outer-sphere processes in both heterogeneous and homogeneous reaction environments.

#### EXPERIMENTAL SECTION

Acetonitrile and methylene chloride (Burdick and Jackson) were dried with calcium hydride, subjected to three freeze-pump-thaw cycles, and normally vacuum distilled before use. DMF, NMF, formamide, DMSO, benzonitrile and acetone (Burdick and Jackson) were degassed and stored in an inert atmosphere dry box.

The tetrabutylammonium hexafluorophosphate (TBAHP) supporting electrolyte was prepared from ammonium hexafluorophosphate (Ozark Mahoning Co.) and tetrabutylammonium bromide (Eastman Kodak) by crystallization from acetone; it was recrystallized twice from ethanol and dried in a vacuum oven. Tetraethylammonium perchlorate (TEAP) (G. F. Smith) was recrystallized thrice from water and dried in a vacuum oven. All solutions were prepared in a dry box under nitrogen. Ferrocene, decamethylferrocene, and cobalticinium hexafluorophosphate were obtained from Strem Chemicals. Decamethylmanganocene was prepared as in ref. 9a, decamethylcobalticinium hexafluorophosphate as in ref. 9b, and dibenzenechromium as in ref. 5c.

The observed "standard" rate constants for electrochemical exchange  $k_{ob}$ , along with the corresponding transfer coefficients,  $\alpha_{ob}$ , were determined at a dropping mercury electrode (mechanically controlled drop time 2 sec, flow rate ca.  $2 \text{ mg sec}^{-1}$ ), by using a.c. polarography as described in refs. 8a and 10. This employed a PAR 173/179 potentiostat, a PAR 175 potential programmer, and a PAR 5204 lock-in amplifier. Frequencies between 100-1400 Hz were employed; the in-phase and quadrature current components were acquired and analyzed using

a LSI 11-23 microcomputer system. Values of  $k_{ob}$  were obtained from the dependence of the ratio of in-phase to quadrature currents as a function of frequency in the conventional manner. The a.c. polarographic data were corrected both for the effects of uncompensated solution resistance ( $R_{us}$ ) as well as for distortions of the time-dependent readout of the lock-in amplifier caused by the necessary use of the low-pass filter.<sup>11</sup> Although positive-feedback iR compensation was employed, the former effect can be significant for  $k_{ob}$  values approaching the measurement limit since small positive values of  $R_{us}$  will inevitably remain. We have recently discussed this matter elsewhere.<sup>8a</sup> Both the above corrections were applied most conveniently with the aid of digitally simulated polarograms using known distorting parameters ( $R_{us}$ , double-layer capacitance, amplifier time constant) for a series of trial values of  $k_{ob}$  in order to obtain the best fit with the observed polarographic response.<sup>8a</sup> Application of these corrections generally acted to increase the derived  $k_{ob}$  values, although usually by factors of 50% or less provided that small lock-in amplifier time constants ( $\leq 0.03$  sec) were employed. The  $k_{ob}$  values reported here are somewhat (ca. 2 fold) higher than those reported in a preliminary communication;<sup>6</sup> the latter were obtained without application of the above corrections and using a longer amplifier time constant (0.15 sec).

Either the oxidized or reduced forms of the redox couple were present in solution (ca. 0.5 - 2 mM), depending on synthetic convenience. Almost all reactions displayed chemical reversibility on the cyclic voltammetric time-scale ( $50-500 \text{ mV sec}^{-1}$ ), as evidenced from equality of the cathodic and anodic peak currents. The exception is the electrooxidation of  $\text{Mn}(\text{Cp}')_2$ , which yielded significantly smaller reverse (cathodic) currents in the most strongly coordinating solvents (DMF, DMSO) at slower scan rates ( $< 0.5 \text{ V sec}^{-1}$ ). Nevertheless, satisfactory a.c. polarograms were obtained for each of these systems.

Temperature control ( $\pm 0.1^\circ\text{C}$ ) was achieved by means of a jacketed cell through which water was circulated from a Braun Melsungen thermostat. All electrode potentials were measured versus an aqueous saturated calomel electrode (s.c.e.) using a cell containing a pair of "fine grade" glass frits so to avoid any contamination of the nonaqueous solution.

## RESULTS AND THEORETICAL ANALYSES

### Rate Constants

Tables I and II contain thermodynamic, structural, and other pertinent parameters for the redox couples and solvents studied in the present work. Values of the formal potential,  $E_f$ , at  $23^\circ\text{C}$  and the reaction entropy,  $\Delta S_{rc}^\circ$ , are given for each redox couple in Table I. The latter were obtained from the temperature derivative of  $E_f$  using a nonisothermal cell arrangement.<sup>12</sup> (Although only representative values of  $E_f$  and  $\Delta S_{rc}^\circ$  are given for most couples due to space limitations, the omitted values can readily be estimated since the solvent dependence of  $E_f$  and  $\Delta S_{rc}^\circ$  are virtually the same for each couple.) Table III contains a summary of the observed rate constants for electrochemical exchange,  $k_{ob}$  ( $\text{cm sec}^{-1}$ ), for each redox couple in the eight solvents studied here. (The gaps in this compilation arise from difficulties in obtaining suitably reliable values of  $k_{ob}$  due to spurious a.c. polarographic behavior associated with adsorption, insolubility, solvent background currents, etc.) The observed transfer coefficients,  $\alpha_{ob}$ , were determined to be uniformly close to 0.50 ( $\pm 0.03$ ). The rate constants were reproducible typically to  $\pm 20\%$ . We also anticipate a similar level of accuracy, except for the largest  $k_{ob}$  values (ca.  $2\text{--}4 \text{ cm sec}^{-1}$ ; *vide supra*), since these are close to the maximum rate constants that can be evaluated using our instrumentation.<sup>8a,10</sup>

The rate parameters in Table III were obtained using  $0.1 \text{ M}$  TBAHP as the supporting electrolyte. It is expected that  $k_{ob}$  will differ from the



"double-layer corrected" standard rate constants,  $k_{\text{corr}}$ , that would be obtained in the absence of the diffuse-layer potential,  $\phi_d$ , by<sup>29</sup>

$$\ln k_{\text{corr}} = \ln k_{\text{ob}} + (Z - \alpha_{\text{corr}}) \phi_d F/RT \quad (1)$$

where  $Z$  is the charge number of the oxidized species and  $\alpha_{\text{corr}}$  is the cathodic work-corrected transfer coefficient,  $[= -(RT/F) d \ln k_{\text{corr}} / dE]$ . Application of Eq. (1) to the present systems by estimating  $\phi_d$  from electrode charge-potential data using the Gouy-Chapman model<sup>30</sup> leads to the prediction that  $k_{\text{corr}}$  should be as much as 5-8 fold smaller than  $k_{\text{ob}}$ , depending on the redox couple. However, several lines of evidence indicate that  $k_{\text{ob}} \approx k_{\text{corr}}$  (at least within ca. 50%), so that the magnitude of the double-layer corrections are markedly smaller than predicted by Eq. (1). Thus  $k_{\text{ob}}$  is virtually independent of the supporting electrolyte concentration, as well as the nature of the cation, over the range 0.05 to 0.5 M. In contrast, ionic strength-dependent values of  $k_{\text{ob}}$ , the variations being roughly in accordance with Eq. (1), are obtained under these conditions for several structurally related anionic redox couples. Further details are given in ref. 31.

The surprisingly small extent of the double-layer corrections for the present systems may be due to the preferential approach of the partially negatively charged cyclopentadiene rings to the electrode surface compensating the effect of the net positive charge of the complex upon the work terms that is anticipated from Eq. (1).<sup>31,32</sup> We have also obtained closely similar (within ca. twofold) values of  $k_{\text{ob}}$  for the present metallocene couples at platinum electrodes using a.c. voltammetry.<sup>8b</sup> All these  $k_{\text{ob}}$  values are markedly larger than some values reported previously;<sup>7a,c</sup> we suspect that the latter suffer from systematic errors associated with solution resistance effects.<sup>8a</sup>

The major thrust of this work is to compare these solvent-dependent rate parameters with the corresponding quantities obtained from theoretical descriptions

of solvent reorganization. We can express the work-corrected rate constant of an exchange reaction either in homogeneous solution or at an electrode surface as<sup>1</sup>

$$k_{\text{corr}} = A \exp[-(\Delta G_{\text{os}}^* + \Delta G_{\text{is}}^*)/RT] \quad (2)$$

where A is a preexponential factor, and  $\Delta G_{\text{os}}^*$  and  $\Delta G_{\text{is}}^*$  are the components of the intrinsic free-energy barrier associated with outer-shell (solvent) and inner-shell (metal-ligand, etc.) reorganization, respectively. Calculated rate constants,  $k_{\text{cal}}$ , were obtained for comparison with the experimental values,  $k_{\text{ob}}$  as follows.

Estimates of  $\Delta G_{\text{is}}^*$  were determined from<sup>33</sup>

$$\Delta G_{\text{is}}^* = 0.5 \epsilon f_{\text{is}} [(\Delta a)/2]^2 \quad (3)$$

where  $\Delta a$  is the change in a given bond distance between the oxidized and reduced forms of the redox couple, and  $f_{\text{is}}$  is the force constant of this bond. The latter is obtained from

$$f_{\text{is}} = 4\pi^2 \nu_{\text{is}}^2 \mu \quad (4)$$

where  $\nu_{\text{is}}$  is the observed frequency ( $\text{sec}^{-1}$ ), and  $\mu$  is the reduced mass of the vibrating bond. For the present redox couples the only significant structural change is the increase (or decrease) of the metal-ring distance. Fortunately, accurate X-ray structural data are available for both oxidized and reduced forms of most reactants studied here so that satisfactory estimates of  $\Delta a$  can be obtained.<sup>13-16</sup> These are listed in Table I along with the literature sources. The corresponding values of  $\nu_{\text{is}}$  are also given in Table I, obtained or estimated from Raman spectroscopic data as described in the footnotes. They refer to the symmetrical stretch of both rings with respect to the metal center, so that  $\mu$  is set equal to the ligand mass. The resulting estimates of  $\Delta G_{\text{is}}^*$  obtained from Eqs. (3) and (5) (Table I) are all small ( $\leq 0.25 \text{ kcal mol}^{-1}$ ), especially

for  $\text{Mn}(\text{Cp}')_2^{+0}$  ( $\Delta G_{is}^* \approx 0.025 \text{ kcal mol}^{-1}$ ). (Note that an inner-shell barrier of  $0.25 \text{ kcal mol}^{-1}$  will act to decrease  $k_{ob}$  by only 50%.)

The outer-shell reorganization energies were calculated from<sup>34</sup>

$$\Delta G_{os}^* = \frac{e^2}{8} \left( \frac{1}{a} - \frac{1}{R_e} \right) \left( \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (5)$$

where  $e$  is the electronic charge,  $a$  is the reactant radius,  $R_e$  is twice the reactant-electrode distance, and  $\epsilon_{op}$  and  $\epsilon_s$  are the optical and static dielectric constants, respectively, for the surrounding solvent. The resulting estimates of  $\Delta G_{os}^*$  for each solvent are given in Table II; they were obtained from the literature values of  $\epsilon_{op}$  and  $\epsilon_s$  also listed in Table II, by assuming that  $a = 3.8 \text{ \AA}$ ,<sup>35</sup> and  $R_e = \infty$ . The last assumption is tantamount to neglecting the reactant-electrode imaging interactions in the transition state<sup>37</sup> (*vide infra*).

In order to obtain calculated rate constants it remains to estimate the preexponential factor  $A$  in Eq. (2). For electrochemical as well as homogeneous reactions it is useful to consider that activation occurs within a previously formed "precursor complex" with the reactant pair (or the reactant-electrode pair) in suitably close proximity.<sup>5b,38-40</sup> One can then write<sup>38</sup>

$$A = K_p \kappa_{el} \nu_n \quad (6)$$

where  $K_p$  is an equilibrium constant for forming the precursor state,  $\kappa_{el}$  is the electronic transmission coefficient and  $\nu_n$  ( $\text{sec}^{-1}$ ) is the nuclear frequency factor. The effective value of  $K_p \kappa_{el}$  will be sensitive to the dependence of  $\kappa_{el}$  upon the reactant-electrode separation.<sup>38,41</sup> Nevertheless, a provisional estimate of  $K_p \kappa_{el}$ , ca.  $6 \times 10^{-9} \text{ cm}$ , is obtained for electrochemical reactions by assuming that  $\kappa_{el}$  approaches unity (i.e., adiabaticity is achieved) only at the plane of closest approach.<sup>41,42</sup>

The values of  $\nu_n$  are of central interest here. This quantity can be determined both by bond vibrations and solvent reorientation, associated with the characteristic frequencies  $\nu_{is}$  and  $\nu_{os}$ , respectively, since these motions comprise the free-energy barrier. A simple formula<sup>43</sup> which has been employed recently<sup>1d</sup> is

$$\nu_n = \left( \frac{\nu_{os}^2 \Delta G_{os}^* + \nu_{is}^2 \Delta G_{is}^*}{\Delta G_{os}^* + \Delta G_{is}^*} \right)^{1/2} \quad (7)$$

Even though  $\Delta G_{os}^* > 20 \Delta G_{is}^*$  for the present reactions (Tables I, II), according to Eq. (7)  $\nu_{is}$  may still provide the predominant contribution to  $\nu_n$  if  $\nu_{os} \ll \nu_{is}$ . Anticipating this possibility (*vide infra*), inserting the typical values  $\Delta G_{is}^* = 0.2 \text{ kcal mol}^{-1}$ ,  $\nu_{is} = 6 \times 10^{12} \text{ sec}^{-1}$  along with  $\Delta G_{os}^*$  (Table II) into Eq. (7) yields  $\nu_n \sim 1.2 (\pm 0.1) \times 10^{12} \text{ sec}^{-1}$ , essentially independent of the solvent. Inserting this along with  $K_p \kappa_{el} = 6 \times 10^{-9} \text{ cm}$  into Eq. (6) yields  $A = 7 \times 10^3 \text{ cm sec}^{-1}$ . This together with the estimates of  $\Delta G_{is}^*$  and  $\Delta G_{os}^*$  (Tables I, II) inserted into Eq. (2) yields the calculated rate constants denoted " $k_{cal}$  (Eq. 7)", listed in Table III. Comparison between the corresponding values of  $k_{cal}$  (Eq. 7) and  $k_{ob}$  (Table III) shows that although the calculated and observed rate constants are generally within ca. 20-fold, the solvent dependence of  $k_{cal}$  is in sharp qualitative disagreement with experiment.

Recent theoretical treatments of solvent reorganization dynamics have emphasized that the effective value of  $\nu_{os}$  can be related closely to the longitudinal (or "constant charge") solvent relaxation time,  $\tau_L$ .<sup>2</sup> This quantity can be extracted from the Debye relaxation time,  $\tau_D$ , determined from dielectric loss measurements using<sup>44</sup>

$$\tau_L = (\epsilon_\infty / \epsilon_s) \tau_D \quad (8)$$

where  $\epsilon_\infty$  is the high-frequency dielectric constant.<sup>45</sup> For relatively "high friction" solvents, say for  $\tau_L \geq 10^{-12}$  sec, the effective outer-shell frequency factor can be expressed for exchange reactions as<sup>2,47</sup>

$$\nu_{os} = \tau_L^{-1} \left( \frac{\Delta G_{os}^*}{4\pi k_B T} \right)^{1/2} \quad (9)$$

where  $k_B$  is the Boltzmann constant. Such relations have not been applied previously to outer-sphere reactions. Nevertheless, a recent study of activationless electron transfer within an extended aromatic system in a series of alcohol solvents indicates that the rates correlate with the solvent relaxation times,<sup>48</sup> and a connection between  $\tau_L^{-1}$  and the solvent dependence of  $k_{ob}$  for some electrochemical reactions has been established empirically.<sup>49</sup>

It is important to note that while Eq. (7) is based on the presumption that the transition-state theory (TST) applies, Eq. (9) describes *deviations* from TST caused by sluggish solvent relaxation. Physically, this corresponds to the system being obliged to recross the transition region many times for reaction to occur since the required *concerted* motion of the surrounding solvent molecules is strongly impeded. Calef and Wolynes<sup>2a</sup> refer to this circumstance as "overdamped" solvent reorientation. They also point out that when this relaxation is relatively fast ( $\tau_L \leq 10^{-12}$  sec), the effective value of  $\nu_{os}$  may be limited by "solvent inertial" effects.<sup>2a</sup> Since this "underdamped" relaxation rate refers to the smooth unimpeded crossing of the system over the transition state, it corresponds to the onset of the TST limit. A simple formula for  $\nu_{os}$  under these conditions is<sup>2a,50</sup>

$$\nu_{os} = (2\pi\tau_{rot})^{-1} (2\epsilon_s \gamma)^{1/2} \quad (10)$$

where  $\tau_{\text{rot}}$  is the solvent rotational relaxation time, estimated from the moment of inertia of the solvent molecules,  $I$ , using

$$\tau_{\text{rot}} = (I/k_B T)^{1/2} \quad (10a)$$

Also,

$$\gamma = \frac{4\pi}{3} \frac{\rho \mu^2}{k_B T} \frac{1}{(\epsilon_s - 1)} \quad (10b)$$

where  $\rho$  is the molar density of the solvent and  $\mu$  is its effective dipole moment. The effective value of  $\nu_{\text{os}}$  when both  $\tau_L$  and  $\tau_{\text{rot}}$  contribute significantly is<sup>2a</sup>

$$\nu_{\text{os}} = (2\pi c \tau_L)^{-1} \left[ 0.5 + 0.5 \left( 1 + \frac{2}{c^2 \epsilon_0 \gamma} \frac{\tau_{\text{rot}}^2}{\tau_L^2} \right)^{1/2} \right]^{-1} \quad (11)$$

where  $c = (k_B T / \pi \Delta G_{\text{os}}^*)^{1/2}$ . Although this definition of  $c$  only applies to "weakly adiabatic" electron transfer (where the electronic matrix coupling element  $H_{12} \leq k_B T$ ), this condition is probably met for most outer-sphere, including electrochemical, reactions.<sup>41,51,52</sup>

Values of  $\nu_{\text{os}}$  estimated from Eq. (9) and (11) are listed for each solvent in Table II. Note that for solvents where  $\tau_L > 1 \times 10^{12} \text{ sec}^{-1}$ ,  $\nu_{\text{os}}(\text{Eq 9}) \approx \nu_{\text{os}}(\text{Eq 11})$ ; otherwise  $\nu_{\text{os}}(\text{Eq 9}) > \nu_{\text{os}}(\text{Eq 11})$ . Rather than inserting these estimates of  $\nu_{\text{os}}$  into the TST expression Eq. (7), we provisionally set  $\nu_{\text{os}} = \nu_{\text{a}}$  (*vide infra*). Combining them with the values of  $\Delta G_{\text{is}}^*$ ,  $\Delta G_{\text{os}}^*$ , and  $K_p^{\text{cal}}$  noted above into Eqs. (2) and (6), yields the calculated rate constants,  $k_{\text{cal}}(\text{Eq 9})$  and  $k_{\text{cal}}(\text{Eq 11})$ , respectively, that are also listed in Table III. In contrast to  $k_{\text{cal}}(\text{Eq 7})$ , these latter rate constants vary with the solvent roughly in accordance with the experimental values,  $k_{\text{ob}}$ , for all five redox couples. Moreover, the values of  $k_{\text{cal}}(\text{Eq 9})$  are within at least 2-3 fold of  $k_{\text{ob}}$  in each solvent.

### Activation Parameters

In order to obtain further insight into the factors influencing  $k_{ob}$  and to provide a more stringent test of the theoretical models, it is desirable to evaluate activation parameters in addition to rate constants at a single temperature. Although electrochemical activation parameters are seldom evaluated, we have repeatedly emphasised their usefulness.<sup>19,53</sup> Table IV lists electrochemical activation parameters for three redox couples,  $Fe(Cp')_2^{+/0}$ ,  $Co(Cp)_2^{+/0}$  and  $Cr(C_6H_6)_2^{+/0}$ , measured in each solvent. The observed activation enthalpies,  $\Delta H_{ob}^*$  (kcal mol<sup>-1</sup>), were obtained from the temperature dependence of  $k_{ob}$  using

$$\Delta H_{ob}^* = -R[d \ln k_{ob}/d(1/T)] \quad (12)$$

The corresponding observed preexponential factors,  $A_{ob}$  (cm sec<sup>-1</sup>), were extracted from  $\Delta H_{ob}^*$  and  $k_{ob}$  by using

$$k_{ob} = A_{ob} \exp(-\Delta H_{ob}^*/RT) \quad (13)$$

Calculated activation enthalpies,  $\Delta H_{cal}^*$ , for comparison with  $\Delta H_{ob}^*$  can be obtained from estimates of the intrinsic enthalpic barrier  $\Delta H_{int}^*$ ; this in turn can readily be obtained from  $\Delta G_{int}^*$  and the intrinsic entropic barrier,  $\Delta S_{int}^*$ , by using

$$\Delta H_{int}^* = \Delta G_{int}^* + T\Delta S_{int}^* \quad (14)$$

As above, we will neglect the inner-shell component and thereby assume that  $\Delta G_{int}^*$  equals the values of  $\Delta G_{os}^*$  obtained from Eq. (5) (Table II). Conventionally,  $\Delta S_{int}^*$  is estimated by assuming that the inner-shell component is zero, and that the outer-shell component,  $\Delta S_{os}^*$ , is given by the dielectric continuum model.<sup>1d</sup> We employ here a modified treatment which yields for electrochemical exchange reactions:<sup>19,54</sup>

$$\Delta S_{\text{int}}^* = \frac{e^2}{8} \left( \frac{1}{a} - \frac{1}{R_e} \right) \left[ \frac{1}{2} \left( \frac{dc_{\text{op}}}{dT} \right) \right] + (\Delta S_{\text{rc}}^* - K_1)/(8n + 4) \quad (15)$$

where  $n$  is the charge number of the reduced form of the redox couple (zero for the present system),  $\Delta S_{\text{rc}}^*$  is the reaction entropy<sup>12</sup> and  $K_1$  is a constant that depends upon the electron-accepting properties of the solvent. Inserting typical values of  $\Delta S_{\text{rc}}^*$  along with literature values of  $\epsilon_{\text{op}}$  and estimates of  $K_1$  into Eq. (15) yields the estimates of  $\Delta S_{\text{int}}^*$  in each solvent given in Table II (see footnotes for details; these are essentially the same for each redox couple in a given solvent). The resulting estimates of  $\Delta S_{\text{int}}^*$  are small, the "optical" component being largely cancelled by the "static" (reaction entropy) component. Therefore from Eq. (14),  $\Delta H_{\text{int}}^* = \Delta G_{\text{int}}^*$ .

In order to obtain calculated activation enthalpies,  $\Delta H_{\text{cal}}^*$ , the temperature dependence of the preexponential factor must also be taken into account. Although  $K_p$  and  $\kappa_{\text{el}}$  [Eq. (6)] are probably temperature independent, according to Eqs. (9) and (11)  $\nu_{\text{os}}$  (and hence  $\nu_n$ ) are temperature dependent since  $\tau_L$  generally decreases with increasing temperature. From the form of Eq. (9), we can write

$$\Delta H_{\text{cal}}^* = \Delta H_{\text{int}}^* - \Delta H_T^* \quad (16)$$

where  $\Delta H_T^* = -R(d \ln \tau_L^{-1} / dT^{-1})$ . Although the required temperature-dependent dielectric loss data are incomplete for the present solvents,  $\Delta H_T^*$  varies from zero to 3 kcal mol<sup>-1</sup> (Table II: note the values in parentheses are estimated).

The resulting values of  $\Delta H_{\text{cal}}^*$  obtained in this manner from Eq. (16) are listed in Table IV for comparison with the corresponding experimental quantities,  $\Delta H_{\text{ob}}^*$ . Also given in Table IV are calculated preexponential factors,  $A_{\text{cal}}$ , obtained from the corresponding values of  $k_{\text{cal}}$  (Eq 11) and  $\Delta H_{\text{cal}}^*$  [cf. Eq. (13)], for comparison with the measured values,  $A_{\text{ob}}$ . Bearing in mind the uncertainties in the values of  $\Delta H_{\text{ob}}^*$  ( $\pm 0.3$  to  $0.5$  kcal mol<sup>-1</sup>) and those in  $A_{\text{ob}}$  (ca. 2-5 fold), the agreement between the calculated and observed activation parameters is



satisfactory. The best agreement is seen for  $\text{Cr}(\text{C}_6\text{H}_6)_2^{+/0}$ ; for the two metallocene couples, typically  $\Delta H_{\text{ob}}^* < \Delta H_{\text{calc}}^*$  and  $A_{\text{ob}} < A_{\text{calc}}$ , although the discrepancies are not large.

## DISCUSSION

### Electrochemical Exchange Kinetics

Although all three sets of calculated rate constants given in Table III are mostly within tenfold of the observed parameters, it is clear that that inclusion of a preexponential factor accounting for the dynamics of solvent reorganization yields a substantially improved description of the solvent-dependent kinetics. This in itself is notable since it suggests that the molecular solvent properties can play an important role in the kinetics of outer-sphere electron transfer beyond influencing the barrier height. We have briefly discussed this matter in a preliminary communication.<sup>6</sup>

It is of interest to reconcile these findings with the anticipated applicability of the alternative frequency factor relations Eqs. (7), (9), (10), and (11). As noted above, Eqs. (7) and (10) are TST expressions, whereas Eqs. (9) and (11) are not. A key issue is the extent to which inner- rather than outer-shell motion controls the preexponential factor. All the present reactions have only small inner-shell barriers. Nevertheless, with the exception of  $\text{Mn}(\text{Cp}')_2^{+/0}$  the values of  $\Delta G_{\text{is}}^*$  are sufficiently large (0.15 - 0.25 kcal mol<sup>-1</sup>) so that according to Eq. (7),  $\nu_{\text{is}}$  constitutes the predominant component of  $\nu_{\text{n}}$  provided that  $\nu_{\text{os}} \leq 1 \times 10^{12}$  sec<sup>-1</sup>. This latter condition is apparently met since TST estimates of  $\nu_{\text{os}}$  in the range ca. 0.5 to  $1 \times 10^{12}$  sec<sup>-1</sup> are obtained from Eq. (10), thereby justifying the assumption  $\nu_{\text{is}} \gg \nu_{\text{os}}$  employed above to obtain  $k_{\text{cal}}$  (Eq 7).

On the other hand,  $\Delta G_{is}^*$  for  $Mn(Cp')_2^{+/0}$  is sufficiently small so that Eq. (7) instead predicts that  $\nu_n$  essentially equals  $\nu_{os}$ , yielding 1.5 to 2 fold smaller predicted values of  $k_{cal}$  (Eq 7) than for the other couples in spite of the slightly lower free-energy barrier for  $Mn(Cp')_2^{+/0}$ . In contrast, the  $k_{ob}$  values for  $Mn(Cp')_2^{+/0}$  are slightly larger than for the other couples in a given solvent (Table III), as expected given the differences in  $\Delta G_{is}^*$  if  $\nu_n$  is the same for each reaction. Indeed, the observed reactivity trend for the homologous series  $Mn(Cp')_2^{+/0} > Fe(Cp')_2^{+/0} > Co(Cp')_2^{+/0}$  (Table III) in each solvent is quantitatively consistent with the differences in  $\Delta G_{is}^*$  noted above. This therefore corroborates the above findings indicating a breakdown in the TST model embodied in Eq. (7).

In contrast, these results are intuitively reasonable on the basis of the model embodied in Eq. (9) since in contrast to the TST approach which predicts that the fastest dynamical component of the barrier will tend to dominate  $\nu_n$ ,<sup>55</sup> such overdamped solvent relaxation is anticipated to dominate  $\nu_n$  when  $\nu_{os}$  is slower than inner-shell motion.

Having exposed a key limitation of Eq. (7), it is nonetheless important to ascertain under what conditions inner-shell motion will dominate  $\nu_n$  even in slowly relaxing solvents ( $\tau_L \gtrsim 10^{-12}$  sec). This question has recently been addressed, and the following approximate inequality derived,<sup>2f</sup> obedience to which denotes conditions for which  $\nu_{os} \approx \nu_n$ :

$$(\Delta G_{is}^* / \Delta G_{int}^*)^{1/2} \nu_{is} \exp(-\Delta G_{is}^* / k_B T) \gtrsim \tau_L^{-1} \quad (17)$$

Inserting the typical values of  $\Delta G_{int}^* = 5 \text{ kcal mol}^{-1}$ ,  $\nu_{is} = 6 \times 10^{12} \text{ sec}^{-1}$ ,  $\Delta G_{is}^* = 0.2 \text{ kcal mol}^{-1}$  into Eq. (17) yields a left-hand-side equal to

$8.5 \times 10^{11} \text{ sec}^{-1}$ . This suggests that TST will not apply for the present reactions in the "slowly relaxing" solvents formamide, NMF, DMSO, and benzonitrile, for which  $\tau_L^{-1} < 8.5 \times 10^{11} \text{ sec}^{-1}$ . The other solvents considered here, acetonitrile, acetone,  $\text{CH}_2\text{Cl}_2$ , and perhaps DMF appear to be "borderline cases" not only with respect to the possible influence of inner-shell motion upon  $v_n$ , but also with regard to solvent inertial effects since the  $\tau_L$  values are sufficiently small ( $\leq 1 \times 10^{-12} \text{ sec}$ ) so that Eqs. (9) and (11) yield significantly different estimates of  $v_{os}$ .

Nonetheless, the simple overdamped solvent model embodied in [Eq. (9)] yields estimates of  $k_{cal}$  that best mimic the solvent-dependent values of  $k_{ob}$  (Table III). In tentatively accepting Eq. (9) as providing the most apt description of the reaction dynamics, it is worth noting that at least the absolute estimates, if not the solvent-dependence, of  $k_{cal}$  contain several uncertainties. Not the least of these is the possibility that the dielectric continuum model [Eq. (5)] may incorrectly estimate the outer-shell barrier. We have recently outlined a phenomenological approach<sup>56</sup> that indicates that this model may significantly underestimate  $\Delta G_{os}^*$ , although the opposite conclusion has been deduced for certain conditions.<sup>57</sup> However, strong evidence favoring the applicability of the dielectric continuum model for estimating  $\Delta G_{os}^*$  for  $\text{Fe}(\text{Cp})_2^{+/0}$  is obtained from its success in rationalizing the solvent-dependence of optically induced electron transfer in binuclear ferrocene complexes,<sup>58,59</sup> including several solvents (acetone, acetonitrile, benzonitrile) employed here for which  $v_{os}$  varies greatly (Table II). A key difference between optical and thermal electron transfer is that only the barrier height, rather than the solvent dynamics, influences the former process. Slightly ( $0.5 - 1 \text{ kcal mol}^{-1}$ ) smaller values of  $\Delta G_{os}^*$  are deduced from Eq. (5) if the electrode imaging term ( $1/R_e$ ) is included,

using reasonable estimates of the reactant-electrode distances.<sup>30</sup> Nevertheless, the calculated enthalpic barriers are close (mostly within 1 kcal mol<sup>-1</sup>) to the observed values, especially for Cr(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>+ / 0</sup> (Table IV), indicating that Eq. (5) is at least approximately applicable to the present systems. This is not too surprising since the reactant's small charge and nonpolar ligands should facilitate the applicability of dielectric continuum treatments.<sup>20,56</sup>

#### Comparison with Homogeneous Self-Exchange Kinetics

Given that the foregoing indicates the importance of solvent relaxation dynamics to electrochemical reactions involving chiefly outer-shell reorganization, it is of interest to ascertain if similar effects can be discerned for related homogeneous exchange processes. Of particular significance are the solvent-dependent bimolecular rate parameters for Fe(Cp)<sub>2</sub><sup>+ / 0</sup> reported by Wahl and coworkers.<sup>5a</sup> Table V contains a summary of their data, including values of  $\Delta H_{ob}^*$  (kcal mol<sup>-1</sup>) and  $A_{ob}$  (M<sup>-1</sup> sec<sup>-1</sup>),<sup>60</sup> as well as  $k_{ob}$  (M<sup>-1</sup> sec<sup>-1</sup>) in eight solvents, four of which were employed for the electrochemical studies (Table III). Alongside these experimental values are summarized the corresponding calculated quantities  $k_{cal}$ ,  $\Delta H_{cal}^*$ , and  $A_{cal}$ . These were obtained using essentially the same procedures to those described above, with the following modifications. A homogeneous precursor formation constant,  $K_p^h$  (M<sup>-1</sup> sec<sup>-1</sup>), was employed in Eq. (6), estimated from the analogous relation<sup>33,38,39</sup>

$$K_p^h = 4\pi N r^2 \delta r_h \quad (18)$$

where  $N$  is Avogadro's number,  $r$  is the internuclear reactant separation in the transition state (taken as  $2a = 7.6 \text{ \AA}$ ), and  $\delta r_h$  is the "reaction zone thickness", taken again as  $0.6 \text{ \AA}$ .<sup>33,42</sup> The value of  $\Delta G_{1s}^*$  (0.3 kcal mol<sup>-1</sup>) is twice the electrochemical value (Table II); the outer-shell barriers are obtained from [cf Eq. (5)]:<sup>34</sup>

$$\Delta G_{os}^* = \frac{e^2}{4} \left( \frac{1}{a} - \frac{1}{R_h} \right) \left( \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (19)$$

where  $R_h$  is the internuclear distance, again taken as  $2a$ . (Note that these estimates of  $\Delta G_{os}^*$  are numerically equal to the above values for electrochemical exchange.) The entropic barriers,  $\Delta S_{int}^*$ , were also set equal to zero, in view of the small electrochemical estimates given in Table II and the incompleteness of the required  $\Delta S_{rc}^*$  data.

If it is assumed, as is conventional, that the preexponential factor is solvent independent, from Eqs. (2) and (19) we can express  $k_{ob}$  as<sup>5b</sup>

$$\ln k_{ob} = K - \frac{e^2}{4RT} \left( \frac{1}{a} - \frac{1}{R_h} \right) \left( \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (20)$$

where  $K$  is a constant which contains both  $A$  and  $\Delta G_{is}^*$ . Wahl et al noted that whereas Eq. (20) predicts a ca. 20 fold variation in  $k_{ob}$  for the solvents listed in Table V (for  $a = 0.5 R_h = 3.8 \text{ \AA}$ ), the experimental values of  $k_{ob}$  are mostly within ca. twofold of each other.<sup>5a</sup> A possible cause of these discrepancies is errors in estimating  $\Delta G_{os}^*$  due to uncertainties in the transition-state geometry as well as in the simple "two-sphere" variant of the continuum model embodied in Eqs. (19) and (20)<sup>1f</sup>. These factors cannot account, however, for the observed *qualitative* inability of Eq. (20) to describe the variations of  $k_{ob}$  upon solvent substitution,<sup>5a</sup> especially given the aforementioned applicability of the continuum model to optical electron transfer within biferrocenes.<sup>59</sup> The values of  $k_{cal}$  given in Table V were obtained instead using the *solvent-dependent* frequency factors estimated from Eq. (9). Comparison between the corresponding values of  $k_{cal}$  and  $k_{ob}$  shows that although generally  $k_{cal} > k_{ob}$  the former successfully mimics the relative solvent-independence of the latter. Thus in most solvents  $k_{cal} = (15 \text{ to } 20) k_{ob}$ ; the only exceptions to this are methanol and  $\text{CH}_2\text{Cl}_2$ .

This surprisingly mild calculated solvent dependence follows from a broad tendency of solvents having larger values of  $\epsilon_{op}$  and hence *smaller*  $\Delta G_{os}^*$  to also exhibit longer relaxation times and hence *smaller* effective values of  $v_{os}$ . The variations in the preexponential and exponential components of  $k_{cal}$  thereby tend to cancel.

The ca. 20-fold discrepancies between  $k_{cal}$  and  $k_{ob}$  may be due in part to systematic errors in calculating the absolute values of  $\Delta G_{os}^*$  and/or  $A$ . If a particular geometry (such as the parallel juxtaposition of a pair of aromatic ligand rings) is preferred in order to provide effective orbital overlap, then  $K_p^h$  and hence  $A$  can be substantially smaller than predicted from Eq. (18).<sup>5b</sup> Judging by the much better agreement between  $k_{ob}$  and  $k_{cal}$  (Eq 9) for the electrochemical reactions (Table III), such steric effects are presumably less important in the heterogeneous reaction environment.

Further evidence suggesting the presence of complicating factors for such homogeneous self-exchange processes is obtained from the ca. 40 fold larger value of  $k_{ob}$  for the self-exchange of  $Cr(C_6H_6)_2^{+/0}$  ( $6 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$  5b) relative to that for  $Fe(Cp)_2^{+/0}$  ( $1.6 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$  5a) in DMSO, even though very similar values are predicted from theoretical considerations and are indeed observed in the heterogeneous environment (Table III). Again in contrast to the electrochemical systems (Table IV) the  $\Delta H_{ob}^*$  values for  $Fe(Cp)_2^{+/0}$  self exchange are substantially (2-4 kcal mol<sup>-1</sup>) smaller than  $\Delta H_{cal}^*$ . Even larger discrepancies are seen between  $A_{ob}$  and  $A_{cal}$ ; typically  $A_{ob} \sim (10^{-3} \text{ to } 10^{-5}) A_{cal}$ . It seems clear that the energetics of the biomolecular reactions contain subtleties, perhaps associated with the approach of the reactant pair, that are absent for the electrochemical exchange reactions.

### Implications for Other Systems

The self-exchange kinetics of several other systems besides  $\text{Fe}(\text{Cp})_2^{+/0}$  have been studied as a function of the solvent,<sup>3,62</sup> although few reports have included a systematic variation in dielectric solvent properties. One objective has been to examine the ability of the dielectric continuum model as embodied in Eq. (20) to predict the dependence of  $k_{\text{ob}}$  upon the solvent. Interestingly, while the solvent dependence of  $k_{\text{ob}}$  for some systems, such as benzonitrile<sup>o/-3c</sup> as well as  $\text{Fe}(\text{Cp})_2^{+/0}$  discussed above, show qualitative deviations from Eq. (20), a few others exhibit tolerable agreement.<sup>62</sup> Examples of the latter behavior are tris-hexafluoroacetylacetonatoruthenium(III)/(II) and related couples ["Ru(hfac)(III)/(II)"],<sup>63</sup> and molecule-cation couples involving *p*-phenylenediamine derivatives.<sup>3e</sup>

These behavioral differences can be rationalized in terms of the present theoretical treatment if inner-shell motion rather than solvent relaxation provides the predominant contribution to the barrier crossing rate, so that  $\nu_n$  is approximately solvent independent. According to Eq. (17), this condition will occur for common polar solvents, for which usually  $\tau_L \leq 2 \times 10^{-12}$  sec, when  $\Delta G_{\text{is}}^* \geq 1$  to 1.5 kcal mol<sup>-1</sup>, (taking the typical values of  $\Delta G_{\text{os}}^* = 5$  kcal mol<sup>-1</sup> and  $\nu_{\text{is}} = 1 \times 10^{13}$  sec<sup>-1</sup>). Although the structural data required to calculate  $\Delta G_{\text{is}}^*$  are lacking, this circumstance is likely for Ru(hfac)(III)/(II) given that significant bond-distance changes are both anticipated and observed for other Ru(III)/(II) couples involving oxygen-donor ligands.<sup>64</sup> Values of  $\Delta G_{\text{is}}^*$  around 0.5 kcal mol<sup>-1</sup> have been estimated empirically for the *p*-phenylenediamine couples;<sup>3e</sup> somewhat larger values, ca. 1 kcal mol<sup>-1</sup>, are obtained from bond-length data.<sup>65</sup> The observed agreement of the solvent-dependent  $k_{\text{ob}}$  values for these systems with the functional form of Eq. (20)<sup>3a</sup> is therefore tentatively

ascribed to the prominent contribution of inner-shell vibrations to  $\nu_n$ . An apparent obedience to Eq. (20), or at least its functional form, can occur even when  $\nu_n \approx \nu_{os}$  if solvents are employed that display comparable values of  $\nu_{os}$  or where the solvent dependence of  $\nu_{os}$  is functionally similar to that of  $\exp(-\Delta G_{os}^*/RT)$ . For example, the former circumstance may account for the approximate success of Eq. (20) for bis-biphenylchromium(I)/(0) self exchange,<sup>5b</sup> since the values of  $\nu_{os}$  do not differ greatly in the pure solvents employed in that study.<sup>66</sup> A more detailed analysis of these and other systems will be given elsewhere.

Irrespective of the details, it is clear that the extent to which the measured kinetics are influenced by solvent relaxation dynamics is sensitive to the nature and extent of the inner-shell barrier as well as to  $\nu_{os}$ . Inner-shell barriers around ca. 0.2 to 2 kcal mol<sup>-1</sup>, associated with the small structural changes that almost inevitably accompany electron transfer, are commonly anticipated even for reactions where solvent reorganization dominates the free-energy barrier. The numerical value of the preexponential factor can therefore be very sensitive to the electronic structure of the redox couple. Unfortunately, the structural data required to estimate  $\Delta G_{is}^*$  are often lacking, especially for organic systems.

These considerations are quite apart from the influence upon  $A_{ob}$  associated with the possible occurrence of nonadiabatic pathways (i.e.,  $\kappa_{el} < 1$ ). In the context of the present discussion, it should be borne in mind that the expression for  $\nu_{os}$  [Eq. (11)] is itself dependent on the reaction adiabaticity.<sup>2a</sup> (*vide supra*) Even though Eq. (11) is appropriate for reaction channels that approach adiabatic ( $\kappa_{el} \sim 1$ ), another relation is appropriate for reactions featuring stronger electronic coupling ("case A" rather than "case B" in ref. 2a).



The overall message is that the solvent sensitivity, as well as the absolute values, of the preexponential factor for electron-transfer reactions that feature chiefly outer-shell reorganization appear to be strongly dependent on a number of parameters, most prominently  $\tau_L$ ,  $\tau_{rot}$ ,  $\nu_{is}$ ,  $\kappa_{el}$ , and  $\Delta G_{is}^*$ . Although hitherto neglected, it is apparent that the first as well as the last three parameters can provide an important influence upon electron-transfer reactivity. A unified theoretical treatment combining each of these various elements is yet to appear. In the meantime, it is hoped that the present work will provide a stimulus for further detailed examinations of solvent-dependent reactivities, both in homogeneous solution and at electrode surfaces.

#### ACKNOWLEDGMENTS

Dr. Tomi Li provided valuable synthetic expertise, Dr. J. C. Smart informed us of some unpublished bond-length data for metallocenes, and Dr. Barbara Behr kindly communicated ref. 49 in advance of publication. We are indebted to Profs. J. T. Hynes and Peter Wolynes for patiently revealing to us some of the mysteries of solvent dynamics. This work is supported by the Office of Naval Research. M.J.W. acknowledges a fellowship from the Alfred P. Sloan Foundation.

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42. The estimate  $K_{pe1} \sim 6 \times 10^{-9}$  cm is obtained from the area contained in a plot of  $\kappa_{e1}$  versus  $(x - x_0)$ , where  $x$  is the reactant-electrode distances and  $x_0$  is this distance at the plane of closest approach, employing the function  $\kappa_{e1} = \exp[-\alpha(x - x_0)]$  with  $\alpha \sim 1.4 \text{ \AA}^{-1}$ .<sup>41</sup>
43. For example, see Slater, N. B.; "Theory of Unimolecular Reactions", Cornell University Press, Ithaca, NY, 1959, pp. 57-9.
44. (a) Frolich, H.; "Theory of Dielectrics", Oxford University Press, 1949; (b) Also see Hubbard, J. B.; J. Chem. Phys. 1978, 68, 1649.
45. The "high-frequency" dielectric constant should be distinguished from the optical dielectric constant,  $\epsilon_{\infty}$  and  $\epsilon_{op}$ , respectively. Typically  $\epsilon_{\infty} \sim 1.5$  to 4 times  $\epsilon_{op}$  for polar liquids.<sup>46</sup>
46. Hill, N. E.; Vaughan, W. E.; Price, A. H.; Davies, M. "Dielectric Properties and Molecular Behavior", Van Nostrand Reinhold, London, 1969, Chapters 1, 4 and 5.
47. Note that Eq. (11) is a special case of relationships given in refs. (2a)-(c), which applies when the free-energy driving force equals zero.
48. (a) Huppert, D.; Kanetz, H.; Kosover, E. M.; Far. Disc. Chem. Soc., 1982, 74, 161; (b) Kosover, E. M.; Huppert, D.; Chem. Phys. Lett. 1983, 96, 433.
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53. (a) Weaver, M. J.; J. Phys. Chem. 1976, 80, 2645; (b) Weaver, M. J.; Israel J. Chem. 1979, 18, 35; (c) Weaver, M. J.; J. Phys. Chem., 1979, 83, 1748; (d) Hupp, J. T.; Weaver, M. J.; J. Electroanal. Chem., 1983, 145, 43.
54. The right-hand-side of the present Eq. (15) is one half that of Eq. (17) in ref. 19; the latter is appropriate for homogeneous self exchange (i.e., for a pair of reactants) while the former is for activation of a single reactant at an electrode. [Also, note that the last term of Eq. 17 in ref. 19 should be  $(\Delta S^\circ - K_1)/(4n + 2)$ ; the division sign was inadvertently omitted in ref. 19.]
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56. Hupp, J. T.; Weaver, M. J.; J. Phys. Chem., in press.
57. Calef, D. F.; Wolynes, P. G.; J. Chem. Phys., 1983, 78, 470.
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59. For biferrocenylacetylene in acetonitrile and benzonitrile, for example, the intervalence charge-transfer energies  $E_{CT}$  ( $= 4\Delta G^\circ_{int}$ ) = 21.4 and 4.25 kcal mol<sup>-1</sup>, respectively, given that  $\Delta G^\circ_{int} = 0.3$  kcal mol<sup>-1</sup> for ferricinium-ferrocene self exchange (i.e., twice the electrochemical value), this yields "experimental"  $\Delta G^\circ_{int}$  values of 5.1 and 4.2 kcal mol<sup>-1</sup> in acetonitrile and benzonitrile. These compare favorably with the corresponding theoretical estimates obtained from Eq. (19) of 5.25 and 3.8 kcal mol<sup>-1</sup>, respectively, by taking  $R_h = 7 \text{ \AA}$  and  $a = 3.8 \text{ \AA}$ . (Note that the effective internuclear distance for biferrocenylacetylene is close to that anticipated for the bimolecular ferricinium-ferrocene system, so that the energetics of the former is a plausible model for those of the latter.) Some significant deviations between the continuum model [Eq. (19)] and the solvent-dependent experimental data are seen, however, for the biferrocene couple.
60. Note that the values of  $\Delta H^\circ_{act}$  in Table V equal the quantities labeled " $E_{act}$ " in ref. 5a., even though somewhat different "activation enthalpies" were quoted (Table V of ref. 5a). These latter quantities were corrected for the anticipated temperature dependence of the collision frequency. This correction is not applied here since it is inappropriate when using the encounter pre-equilibrium treatment.
61. The discrepancies between  $k_{cal}$  and  $k_{ob}$  are smaller for  $\text{Fe}(\text{Cp}')_2^{+/0}$  than noted in Table V for  $\text{Fe}(\text{Cp})_2^{+/0}$ , at least in acetonitrile, since  $k_{cal}$  for the former is eightfold larger than for the former. Methyl substitution, however, has only a more modest effect upon the electrochemical exchange rates for cobalticinium-cobaltocene (Table III).

62. For brief summary of the literature results, see refs. 5a and 63.
63. Chan, M-S.; Wahl, A. C.; J. Phys. Chem. 1982, 86, 126.
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65. (a) DeBoer, J. L.; Vos, A.; Acta. Cryst. ~~1972~~, B28, 835; (b) Ikemoto, I.; Acta. Cryst. ~~1979~~, B35, 2264.
66. The mixed-solvent data in ref. 5b may be complicated by selective solvation effects. Of the four pure solvents in ref. 5b; benzonitrile, DMSO, DMF, and propylene carbonate; the  $\nu_{\text{as}}$  values given by Eq. (11) differ by 2-fold or less (Table III;  $\nu_{\text{as}}$  for the last solvent is calculated from data in ref. 67 to be  $3^{\text{as}} \times 10^{12} \text{ sec}^{-1}$ ).
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TABLE I Relevant Properties of Metallocene and Metal Arene Redox Couples

Redox Couple <sup>a</sup>	Solvent <sup>b</sup>	E <sub>f</sub> <sup>c</sup> mV vs sce	$\Delta S_{rc}^{\circ}$ <sup>d</sup> cal deg <sup>-1</sup> mol <sup>-1</sup>	D <sup>e</sup> cm <sup>2</sup> sec <sup>-1</sup>	$\Delta a^h$ $\lambda$	$\nu_{is}^j$ sec <sup>-1</sup>	$\Delta G_{is}^{*n}$ kcal mol <sup>-1</sup>
Fe(Cp') <sub>2</sub> <sup>+ / o</sup>	Acetonitrile	- 80	~ 11	1.3x10 <sup>-5</sup> f	-0.035	6.4x10 <sup>12j</sup>	0.15
	Acetone	- 15	14	1.5x10 <sup>-5</sup> f			
	Cl <sub>2</sub> Cl <sub>2</sub>	-130	5	1.3x10 <sup>-5</sup> f			
	NMF	- 75	~ 3	1.4x10 <sup>-6</sup> f			
	DMF	60	12	7.7x10 <sup>-6</sup> f			
	DMSO	- 40	8.5	3.2x10 <sup>-6</sup> f			
Fe(Cp) <sub>2</sub> <sup>+ / o</sup>	Acetonitrile	425	11.5		9.10 <sup>12k</sup>		~0.15
Co(Cp') <sub>2</sub> <sup>+ / o</sup>	Acetonitrile	-1510		1.3x10 <sup>-5</sup> g	0.045	6x10 <sup>12l</sup>	0.22
	DMF	-1395		8x10 <sup>-6</sup> g			
Co(Cp) <sub>2</sub> <sup>+ / o</sup>	Acetonitrile	-905	17	1.8x10 <sup>-5</sup> g	~0.05	9x10 <sup>12l</sup>	~0.25
	DMF	-830	16	7x10 <sup>-6</sup> g			
	Formamide	-1045	4.5	4.8x10 <sup>-6</sup> g			
Mn(Cp') <sub>2</sub> <sup>+ / o</sup>	Acetonitrile	-540		1.5x10 <sup>-5</sup> f	-0.014	6x10 <sup>12l</sup>	0.025
	DMF	-490		7.5x10 <sup>-6</sup> f			
Cr(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub> <sup>+ / o</sup>	Acetonitrile	-770	16	1.3x10 <sup>-5</sup> g	~0.045	8.5x10 <sup>12m</sup>	~0.2
	DMF	-710	16.5	8x10 <sup>-6</sup> g			
	Formamide	-930	2	5x10 <sup>-6</sup> g			
	Benzonitrile	-795	5	2.4x10 <sup>-6</sup> g			

# Footnotes to Table I

<sup>a</sup> Cp = cyclopentadiene, Cp' = pentamethylcyclopentadiene

<sup>b</sup> NMR = N-methylformamide, DMF = N,N-dimethylformamide, DMSO = dimethylsulfoxide

<sup>c</sup> Formal potential of redox couple, obtained by using a.c. polarography or cyclic voltammetry in indicated solvent containing 0.1 M tetrabutylammonium hexafluorophosphate. Potentials measured against aqueous saturated calomel electrode in contact with nonaqueous electrolyte.

<sup>d</sup> Reaction entropy of redox couple,<sup>11</sup> obtained from temperature dependence of  $E_f$  using nonisothermal cell arrangement as detailed in ref. 12.

<sup>e</sup> Diffusion coefficient for either oxidized or reduced form of redox couple as indicated, determined from d.c. polarography.

<sup>f</sup> For reduced form.

<sup>g</sup> For oxidized form.

<sup>h</sup> Change in metal-ring bond distance between oxidized and reduced forms of redox couple. Obtained from corresponding metal-carbon bond distances,  $a_{ox}$  and  $a_{red}$  ( $\text{\AA}$ ), determined from X-ray crystallography as follows:  $\text{Fe}(\text{Cp}')_2$ ;  $a_{ox} = 2.097$ ,  $a_{red} = 2.050$ ;  $\text{Co}(\text{Cp}')_2$ ;  $a_{ox} = 2.049$ ,  $a_{red} = 2.105$ ;  $\text{Fe}(\text{Cp})_2$ ;  $a_{ox} = 2.029$ ,  $a_{red} = 2.096$ ;  $\text{Mn}(\text{Cp}')_2$ ;  $a_{ox} = 2.130$ ,  $a_{red} = 2.112$ ;  $\text{Cr}(\text{C}_6\text{H}_6)_2$ ;  $a_{ox} = 2.08$ ,  $a_{red} = 2.13$ .

<sup>i</sup> Average frequency of inner-shell (metal-ring) vibration ( $\text{sec}^{-1}$ ) for oxidized and reduced forms of redox couple, from corresponding totally-symmetrical Raman frequency,  $\nu_R$  ( $\text{cm}^{-1}$ ), measured or estimated as noted.

<sup>j</sup> Estimated from corresponding value of  $\nu_R$  for  $\text{Fe}(\text{Cp})_2$  (300  $\text{cm}^{-1}$  13a) by accounting for additional mass of methyl groups assuming an identical force constant.

<sup>k</sup> From experimental value of  $\nu_R$  ( $\approx 300 \text{ cm}^{-1}$  13a).

<sup>l</sup> Estimated from value for  $\text{Fe}(\text{Cp}')_2$  or  $\text{Fe}(\text{Cp})_2$ , by noting relation between  $\nu_R$  and metal-carbon bond distance. 13a

<sup>m</sup> From experimental value of  $\nu_R$  ( $\approx 275 \text{ cm}^{-1}$  16).

<sup>n</sup> Inner-shell electrochemical intrinsic barrier, from values of  $\Delta s$  and  $\nu_{is}$  using Eqs. (3) and (4). Values estimated to be accurate at least  $\pm 20\%$ , except for  $\text{Co}(\text{Cp})_2$  and  $\text{Cr}(\text{C}_6\text{H}_6)_2$ , ca  $\pm 30\text{--}50\%$ .



TABLE II Solvent and Related Properties at 25°C

Solvent	$\epsilon_{op}^a$	$\epsilon_s^b$	$\Delta G_{os}^{*c}$ kcal mol <sup>-1</sup>	$\Delta S_{int}^{*d}$ cal deg <sup>-1</sup> mol <sup>-1</sup>	$\tau_D^e$ 10 <sup>-12</sup> sec	$\tau_L^k$ 10 <sup>-12</sup> sec	$\nu_{op}^l$ (Eq 9) 10 <sup>12</sup> sec <sup>-1</sup>	$\nu_{os}^m$ (Eq 11) 10 <sup>12</sup> sec <sup>-1</sup>	$\Delta H_f^o$ kcal mol <sup>-1</sup>
acetonitrile	1.80	37.5	5.75	-1.5	3.3 <sup>f</sup>	±0.2	4.5	1.3	1.1
acetone	1.84	20.7	5.4	-1.0	3.3 <sup>g</sup>	0.3	3.0	0.8	1.0
CH <sub>2</sub> Cl <sub>2</sub>	2.03	9.0	4.2	~4	1.5 <sup>h</sup>	~0.4	1.9	0.55	(~1)
formamide	2.09	110	5.1	1.5	37 <sup>i</sup>	2.4	0.35	0.35	~3.0
HF	2.04	182	5.25	-0.5	123 <sup>j</sup>	3.6	0.24	0.22	~2.5
HF	2.04	36.7	5.05	-0.5	11.0 <sup>k</sup>	1.3	0.65	0.3	~1.0
DMSO	2.18	46.7	4.7	-1.5	19.6 <sup>l</sup>	2.3	0.34	0.3	(~1.5)
benzonitrile	2.33	25.2	4.2	~1	38 <sup>j</sup>	5.7	0.13	0.13	(~1.5)

Footnotes

Optical dielectric constant, from refractive index data given in ref. 17.

Static (i.e. zero frequency) dielectric constant, from refs. 17 and 18.

Outer-shell intrinsic free energy of activation in given solvent, from Eq. (5) with  $a = 3.8 \text{ Å}$  and  $R = \infty$  (see text), using listed values of  $\epsilon_{op}$  and  $\epsilon_s$ .

Intrinsic entropy of activation in given solvent, from Eq. (15) with  $a = 3.8 \text{ Å}$  and  $R = \infty$  (see text). Values of  $\epsilon_{op}$  ( $d\epsilon_{op}/dT$ ) taken from ref. 17. Values of  $\Delta S_{int}^*$  as follows: acetonitrile, 13 cal deg<sup>-1</sup> mol; acetone, 15; CH<sub>2</sub>Cl<sub>2</sub>, 5; formamide, 3; HF, 4; DMF, 14; DMSO, 10; benzonitrile, ~10. Values of  $K_1$  taken as zero except in formamide (~7 cal deg<sup>-1</sup> mol<sup>-1</sup>), and NMR (-5) (see text and refs. 19 and 20 for details).

Debye relaxation time, obtained from dielectric loss measurements in references cited.

Ref. 21.

Ref. 22.

[Continued on next page]

Footnotes to Table II Continued

<sup>h</sup> Ref. 23.

<sup>i</sup> Ref. 24.

<sup>j</sup> Ref. 25.

<sup>k</sup> Longitudinal solvent relaxation time, determined from corresponding values of  $\tau_D$  with values of  $\epsilon_\infty$  and  $\epsilon_s$  given in references cited for  $\tau_D$ , by using Eq. (8).

<sup>l</sup> Solvent preexponential factor, obtained from values of  $\tau_L$  and  $\Delta G_{OS}^\ddagger$  by using Eq. (9).

<sup>m</sup> Solvent preexponential factor, obtained from Eq. (11) using listed values of  $\tau_L$ ,  $\epsilon$ , and  $\Delta G_{OS}^\ddagger$ , and estimates of  $\tau_{rot}$  and  $\gamma_\epsilon$  evaluated from Eqs. (10a) and (10b), respectively. These estimates of  $\tau_{rot}$  and  $\gamma_\epsilon$ , respectively, for each solvent are as follows: acetonitrile, 0.45 psec, 4.5; acetone, 0.9 psec, 1.9;  $CH_2Cl_2$ , 0.2 psec, 0.4; formamide, 0.5 psec, 5.7; NMR, 0.65 psec, 5.0; DMF, 0.85 psec, 3.8; DMSO, 0.6 psec, 4.3; benzonitrile, 1.0 psec, 3.2.

<sup>n</sup> Enthalpy of activation associated with longitudinal solvent relaxation; determined from  $\Delta H_T^\ddagger = -R \left( \frac{d \ln \tau_L}{dT} \right)$ , where  $\tau_L$  is evaluated from Eq. (8). Values obtained from temperature-dependent dielectric loss data using literature sources listed in  $\tau_D$  column. Values in parenthesis are estimated.

TABLE III Comparison between Experimental and Calculated Rate Constants ( $\text{cm sec}^{-1}$ ) for Electrochemical Exchange at 23°C

Solvent	Calculated Rate Constants, $k_{\text{cal}}$		Observed Rate Constants, $k_{\text{ob}}^d$			
	(Eq. 7) <sup>a</sup>	(Eq. 9) <sup>b</sup> (Eq. 11) <sup>c</sup>	$\text{Mn}(\text{Cp}')_2^{+/0}$	$\text{Fe}(\text{Cp}')_2^{+/0}$	$\text{Co}(\text{Cp}')_2^{+/0}$	$\text{Cr}(\text{C}_6\text{H}_6)_2^{+/0}$
Acetonitrile	0.30	1.6 0.5	$\sim 4$	e	$\sim 3.5$	$\sim 4$
Acetone	0.55	2.0 0.5	$\sim 4$	$\sim 3.5$	$\sim 3$	2.5
$\text{CH}_2\text{Cl}_2$	4.0	10 2.8			$\geq 2$	
Formamide	0.9	0.4 0.35	f		0.55	0.55
NMF	0.7	0.20 0.2	f	0.9	0.8	0.65
DHF	1.0	0.6 0.35	$\sim 2$	$\sim 2$	$\sim 1.5$	$\sim 1.2$
DMSO	2.5	0.7 0.65	0.9	0.85	0.75	0.5
Benzonitrile	4.2	0.65 0.6		0.4	0.25	0.3

Footnotes

<sup>a</sup> Rate constant ( $\text{cm sec}^{-1}$ ) calculated from Eqs. (2), (5), and (6) with  $\Delta G_{12}^\ddagger = 0$ ,  $\Delta G_{10}^\ddagger$  as given in Table II,  $K_{\text{p,cl}} = 0.6$ ,  $v_n$  obtained from Eq. (7), with  $\Delta G_{12}^\ddagger = 0.2 \text{ kcal mol}^{-1}$ ,  $v_{12} = 6 \times 10^{12} \text{ sec}^{-1}$ , and  $v_{08} \ll v_{12}$  (see text).

<sup>b</sup> As footnote a, but with  $v_n$  set equal to  $v_{08}$  obtained from Eq. (9) (Table II).

<sup>c</sup> As footnote a, but with  $v_n$  set equal to  $v_{08}$  obtained from Eq. (11) (Table II).

<sup>d</sup> Observed rate constant ( $\text{cm sec}^{-1}$ ) obtained for stated redox couple in solvent indicated, containing 0.1 M TRAP. Values reproducible to ca  $\pm 20\%$ .

<sup>e</sup> Measurement precluded due to spurious a.c. polarographic behavior.

<sup>f</sup> Measurement precluded due to insufficient solubility of metallocene.

TABLE IV Comparison between Experimental and Calculated Activation Parameters for Electrochemical Exchange

Solvent	$\Delta H_{cal}^*$ <sup>a</sup>	$A_{cal}^b$	$\Delta H_{ob}^*$ <sup>c</sup>	$A_{ob}^d$ <sup>+/-</sup>	$\Delta H_{ob}^*$ <sup>c</sup>	$A_{ob}^d$ <sup>+/-</sup>	$\Delta H_{ob}^*$ <sup>c</sup>	$A_{ob}^d$ <sup>+/-</sup>
			$Fe(Cp')_2$		$Co(Cp)_2$		$Cr(C_6H_6)_2$	
Acetonitrile	6.5	$9 \times 10^4$			4.5	$6 \times 10^3$	6.2	$1 \times 10^5$
Acetone	6.1	$6 \times 10^4$	4.5	$8 \times 10^3$	5.0	$1 \times 10^4$	7.5	$5 \times 10^5$
Formamide	5.5	$5 \times 10^5$			6.2	$2 \times 10^4$	7.5	$1.5 \times 10^5$
NMF	7.5	$6 \times 10^4$					6.0	$2 \times 10^4$
DMF	5.8	$1.0 \times 10^6$	4.5	$5 \times 10^3$	5.0	$8 \times 10^3$	5.5	$1.5 \times 10^4$
DMSO	~6	$2 \times 10^4$	5.2	$6 \times 10^3$	5.5	$8 \times 10^3$	5.8	$8 \times 10^3$
Benzonitrile	~6	$2 \times 10^4$					5.5	$4 \times 10^3$

Footnotes

<sup>a</sup> Calculated enthalpy of activation ( $kcal\ mol^{-1}$ ), obtained from Eqs. (14) and (16), with  $\Delta S_{int}^*$  and  $\Delta H_T^*$  from Table II, and  $\Delta G_{int}^*$  assumed equal to  $\Delta G_{os}^*$ , from Table II.

<sup>b</sup> Calculated preexponential factor ( $cm\ sec^{-1}$ ), obtained from  $\Delta H_{cal}^*$  and  $k_{cal}$  (Eq. 11) (Table III) using  $A_{cal} = k_{cal} \exp(\Delta H_{cal}^*/RT)$ .

<sup>c</sup> Experimental enthalpy of activation ( $kcal\ mol^{-1}$ ) for given redox couple, obtained from temperature derivative of  $k_{ob}$  by using Eq. (12). Uncertainties in listed values typically 0.3 - 0.5  $kcal\ mol^{-1}$ .

<sup>d</sup> Experimental preexponential factor ( $cm\ sec^{-1}$ ) for given redox couple, obtained from values of  $\Delta H_{ob}^*$  and  $k_{ob}$  (Table III). Uncertainties in listed values typically 2-5 fold.

TABLE V Comparison between Experimental and Calculated Rate Parameters for Ferricinium-Ferrocene Self Exchange

Solvent	$\Delta G_{cs}^{\ddagger a}$ kcal mol <sup>-1</sup>	$\nu_{os}^b$ 10 <sup>12</sup> sec <sup>-1</sup>	$k_{cal}^{\ddagger}$ M <sup>-1</sup> sec <sup>-1</sup>	$\Delta H_{cal}^{\ddagger h}$ kcal mol <sup>-1</sup>	$A_{cal}^{\ddagger i}$ M <sup>-1</sup> sec <sup>-1</sup>	$k_{ob}^j$ M <sup>-1</sup> sec <sup>-1</sup>	$\Delta H_{ob}^{\ddagger k}$ kcal mol <sup>-1</sup>	$A_{ob}^{\ddagger l}$ M <sup>-1</sup> sec <sup>-1</sup>
Methanol	5.85	0.12 <sup>c</sup>	1.5x10 <sup>6</sup>	~9	~5x10 <sup>12</sup>	6.0x10 <sup>6</sup>	3.0	1x10 <sup>9</sup>
Acetonitrile	5.75	4.5	7x10 <sup>7</sup>	7.2	1.5x10 <sup>13</sup>	5.3x10 <sup>6</sup>	5.0	2.5x10 <sup>10</sup>
Nitromethane	5.4	3.5 <sup>d</sup>	1.0x10 <sup>8</sup>	6.5	6x10 <sup>12</sup>	5.8x10 <sup>6</sup>	4.0	5x10 <sup>9</sup>
Acetone	5.4	3.0	8.5x10 <sup>7</sup>	6.7	7x10 <sup>12</sup>	4.6x10 <sup>5</sup>	4.8	1.5x10 <sup>10</sup>
DMSO	4.7	0.34	3.2x10 <sup>7</sup>	~6.5	~2x10 <sup>12</sup>	1.6x10 <sup>6</sup>		
Nitrobenzene	4.2	0.35 <sup>e</sup>	7.7x10 <sup>7</sup>	~6	~2x10 <sup>12</sup>	2.3x10 <sup>6</sup>	2.3	1x10 <sup>8</sup>
CH <sub>2</sub> Cl <sub>2</sub>	4.2	1.9	4.1x10 <sup>8</sup>	~6	~1x10 <sup>13</sup>	4.3x10 <sup>6</sup>	2.0	1.3x10 <sup>8</sup>
(CH <sub>2</sub> Cl) <sub>2</sub>	4.15	0.45 <sup>f</sup>	1.1x10 <sup>8</sup>	6.0	3x10 <sup>12</sup>	4.3x10 <sup>6</sup>	2.0	1.3x10 <sup>8</sup>

Footnotes

<sup>a</sup> Outer-shell free energy of activation, determined from Eq. (19) with  $a = 3.8 \text{ \AA}$ ,  $R_h = 2a$ , using values of  $\epsilon_{op}$  and  $\epsilon_g$  taken from refs. 17, 18.

<sup>b</sup> Solvent preexponential factor, obtained from Eq. (9) using values of  $\tau_L$  noted in Table II, determined from  $\tau_D$ ,  $\epsilon_g$ ,  $\epsilon_{\infty}$  [Eq. (8)] from source noted.

<sup>c</sup> Ref. 26.

<sup>d</sup> Ref. 27.

<sup>e</sup> Ref. 25.

<sup>f</sup> Ref. 28.

<sup>g</sup> Rate constant calculated from Eqs. (2) and (6) with  $K_p^h = 0.262 \text{ M}^{-1}$  [from  $K_p^h = 4\pi N r^2 \delta r$ , with  $r = 7.6 \text{ \AA}$  (1.e. 2a), and  $\delta r = 6 \times 10^{-9} \text{ cm}$  (see text)], and using listed values of  $\Delta G_{os}^{\ddagger}$  and  $\nu_{os}$ . With  $\Delta G_{int}^{\ddagger} = \Delta G_{os}^{\ddagger} + 0.3 \text{ kcal mol}^{-1}$ .

Footnotes to Table V Continued

- <sup>h</sup> Calculated enthalpy of activation, obtained from  $\Delta H_{cal}^{\ddagger} = \Delta G_{os}^{\ddagger} + \Delta G_{cal}^{\ddagger} + T\Delta S^{\ddagger} + \Delta H_{cal}^{\ddagger}$ , with  $\Delta G_{cal}^{\ddagger} = 0.3$  kcal mol<sup>-1</sup>,  $\Delta S^{\ddagger} = 0$ , and  $\Delta H_{cal}^{\ddagger}$  determined or estimated from temperature dependence of  $v_{os}$  (see Table II and references cited for  $v_{os}$ ).
- <sup>i</sup> Calculated preexponential factor, obtained from corresponding values of  $k_{cal}$  and  $\Delta H_{cal}^{\ddagger}$ .
- <sup>j</sup> Observed rate constant for homogeneous  $Fe(Cp)_2^{+/0}$  self exchange at 25°C, from ref. 4.
- <sup>k</sup> Observed enthalpy of activation, equal to Arrhenius activation energy, from ref. 4.
- <sup>l</sup> Observed preexponential factor, obtained from corresponding values of  $k_{ob}$  and  $\Delta H_{ob}^{\ddagger}$ .